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UNITED STATES SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT WE, ROLAND BRUNNER, HELMUT SCHWENK, JOHANN ZACH, all German citizens, reside at Berg 1, D-84367 Reut, Germany; Robert-Koch-Strasse 209, D-84489 Burghausen, Germany; Gambacher Weg 8, D-84347 Pfarrkirchen, Germany, have invented certain new and useful improvements in a

PROCESS FOR THE WET CHEMICAL TREATMENT OF SEMICONDUCTOR WAFERS
of which the following is a specification.

66220T-46952460

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, in particular a process for the cleaning of silicon semiconductor wafers.

2. The Prior Art

A treatment process of this type has been described, for example, by M. Meuris et al. in *Solid State Technology*, July 1995, p. 109.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process by which metallic impurities and particles can be removed particularly effectively from semiconductor wafers.

The above object is achieved according to the present invention by providing a process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, wherein the semiconductor wafers are

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firstly treated with an aqueous HF solution, then with an aqueous O_3 solution and finally with water or an aqueous HCl solution, these treatments forming a treatment sequence.

It has been found that the object is achieved by this treatment sequence, which does not need to be interrupted by rinsing with water or another treatment liquid and is carried out exclusively at a pH which is lower than pH 7. The treatment according to the invention with the treatment liquids indicated is performed in treatment baths. It is preferable to circulate the treatment liquid, that is to take some of this liquid from the corresponding treatment bath and return it back after having been filtered. This saves on outlay for the required chemicals and for deionized water. The addition of fresh water or other liquids to the treatment baths is to be avoided since, when valves are opened, pressure impulses are created and particles can be introduced into the treatment baths. The treatment according to the invention is therefore different from a rinsing treatment, in which fresh treatment liquid is supplied continuously or at intervals.

The treatments include treating the semiconductor wafers firstly in a bath with an aqueous HF solution, then in a bath with an aqueous O_3 solution and finally in a bath with water or an aqueous HCl solution, form a treatment sequence B_2 . Sequence B_2 may be preceded by a treatment B_1 of the semiconductor wafers in a bath

with an aqueous SCl solution. An SCl solution contains NH_4OH and H_2O_2 or TMAH (= tetramethylammonium hydroxide) and H_2O_2 is preferred. The treatment sequence B_2 may also be followed by a treatment B_3 of drying the semiconductor wafers. The drying treatment is preferably carried out using the centrifugal, hot water, isopropanol or marangoni principle.

It is particularly preferable to arrange the sequencing of the treatment of the semiconductor wafers according to the term $m^*(B_1 + B_2) + B_3$, with m being an integer number. The treatment B_1 and the treatment sequence B_2 are carried out in succession, and this takes place m times, before the drying treatment B_3 is performed.

The aqueous HF solution used in the treatment sequence B_2 preferably contains HF in a concentration of from 0.001% to 2% by weight and optionally HCl in a concentration of up to 2% by weight and optionally a surfactant. A mixture of alkylbenzenesulfonate and fatty amine polyglycol ethers in a concentration of 0.001% to 2% by weight is particularly preferred as a surfactant additive. The aqueous O_3 solution used in the treatment sequence B_2 preferably contains O_3 in a concentration of from 1 to 30 ppm and optionally HF in a concentration of from 0.0001% to 2% by weight and is optionally exposed to megasonic waves. The liquid used last in the treatment sequence B_2 is water or an aqueous HCl solution, which preferably contains HCl in a concentration of from 0.001% to 10% by

weight. The liquid may optionally contain O_2 and optionally be exposed to megasonic waves. The temperature of the bath is preferably at a temperature of from room temperature to $80^{\circ}C$.

All percents by weight are based upon the total solution weight.

Other objects and features of the present invention will become apparent from the following detailed description considered in connection with the accompanying examples which disclose embodiments of the present invention. It should be understood, however, that the examples are designed for the purpose of illustration only and not as a definition of the limits of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The comparison below of an invention example with comparative examples shows the advantageous effect of the present invention.

The table contains the results (3 sigma values) of conventional counts of particles of specific size (LPD = light point defects), which were in each case carried out on 20 polished semiconductor wafers after a wet chemical treatment sequence and drying which was the same for all the semiconductor wafers.

The example (B) comprised the treatment sequence: HF bath, deionized water/ozone bath, HCl bath with megasonic exposure.

Comparative Example 1 (C1) comprised the treatment sequence: HF bath, deionized water/ozone bath, rinsing with deionized water outside the bath.

Comparative Example 2 (C2) comprised the treatment sequence: HF bath, deionized water/ozone bath with subsequent rinsing using deionized water in the bath and megasonic exposure.

LPD (μ M)	>0.3	>0.2	>0.16	>0.12
	Number	Number	Number	Number
B	3	7	30	480
C1	4	13	50	550
C2	10	50	140	550

Accordingly, while a few embodiments of the present invention have been shown and described, it is to be understood that many changes and modifications may be made thereunto without departing from the spirit and scope of the invention as defined in the appended claims.